CHEMISTRY
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Accepted Article

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To be cited as: *Chem. Eur. J.* 10.1002/chem.201701270

Link to VoR: http://dx.doi.org/10.1002/chem.201701270

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FULL PAPER

Synthesis of Mono-, Bis- and Tris(pentafluoroethyl)tin Derivatives, $(C_2F_5)_{4-n}SnX_n$ (X = Ph, Me, Cl, Br, Cp; n = 1-3)

Johannes Klösener, Markus Wiesemann, Mark Niemann, Beate Neumann, Hans-Georg Stammler and Berthold Hoge*

Dedicated to Prof. Dr. Helge Willner on the occasion of his 70th birthday

Abstract: For (pentafluoroethyl)phenylstannanes, $(C_2F_5)_{4-n}SnPh_n$ (n = 1-3), and dimethylbis(pentafluoroethyl)stannane, $(C_2F_5)_2SnMe_2$, a high yield synthesis was developed by the use of LiC_2F_5 as a C_2F_5 transfer reagent. The treatment of these products with gaseous hydrogen chloride or hydrogen bromide afforded $(C_2F_5)_{4-n}SnX_n$ (X = Cl, Br; n = 1-3) in good yields. The (pentafluoroethyl)stannanes were fully characterized by ^1H, ^{13}C, ^{19}F and ^{119}Sn NMR, IR spectroscopy and mass spectrometry.

The treatment of the (pentafluoroethyl)tin halides $(C_2F_5)_{4-n}SnX_n$ with 1,10-phenanthroline (phen) led to the formation of the corresponding octahedrally coordinated complexes $[(C_2F_5)_{4-n}SnX_n(phen)]$, the structures of which were elucidated by X-ray diffraction analyses.

The bromostannane $(C_2F_5)_3SnBr$ was reacted with sodium cyclopentadienide to give the (η^1-cyclopentadienyl)-tris(pentafluoroethyl)stannane, $(C_2F_5)_3SnCp$. A single crystal was grown by in situ crystallization and used for X-ray diffraction analysis.

The coupling constants $^1J(^{119}Sn,^{13}C)$ and $^2J(^{119}Sn,^{19}F)$ of all new stannanes are strongly correlated and sensitive to the substitution pattern at the tin atom. For both coupling constants a negative sign could be assigned.

Introduction

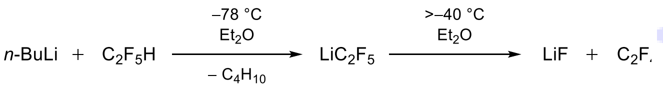
The replacement of electron donating alkyl by electron withdrawing perfluoroalkyl groups has dramatic effects on the electronic nature of an organoelement compound and usually is accompanied by a significant stabilization of these types of compounds. As a consequence, electron deficient tin compounds exhibit an increased Lewis acidity compared to alkylstannanes. (Trifluoromethyl)stannane derivatives, $(CF_3)_{4-n}SnX_n$ (X = F, Cl, Br, I; n = 0-3), were synthesized and studied extensively by *Eujen et al.*[1] The treatment of $SnBr_4$ with the toxic reagents $Cd(CF_3)_2$ or $Hg(CF_3)_2$ led to a series of different bromo(trifluoromethyl)-stannanes, $(CF_3)_{4-n}SnBr_n$ (n = 0-3) as well as $Sn(CF_3)_4$ (Scheme 1). However, these (trifluoromethyl)stannanes are highly sensitive towards difluorocarbene elimination and dismutation reactions.[2]

$$SnBr_4 + Cd(CF_3)_2{\cdot}D \longrightarrow \underset{(n = 0\text{-}3;\ D = \text{diglyme})}{(CF_3)_{4-n}SnBr_n}$$

Scheme 1. Synthesis of bromo(trifluoromethyl)stannanes, $(CF_3)_{4-n}SnB$ (n = 1-3) and tetrakis(trifluoromethyl)stannane $Sn(CF_3)_4$.

Cullen et al. investigated the thermal decomposition c trimethyl(perfluoroalkyl)stannanes, R^fSnMe_3 (R^f = CF_3, C_2F $CF(CF_3)_2$). In contrast to trifluoromethyl and heptafluoroisopropy substituted stannanes, which decompose at 150 °C, more tha 90 % of the trimethyl(pentafluoroethyl)stannane, $(C_2F_5)SnMe$ could be recovered after heating for 72 hours at 200 °C.[3] Thi illustrates the particularly high thermal stability c (pentafluoroethyl)stannanes. However, little work has bee published on (pentafluoroethyl)tin halides.

The first (pentafluoroethyl)stannanes $(C_2F_5)SnR_3$ (R = Me, E Ph) were synthesized in yields up to 22 % by reacting hexaalky or hexaphenyldistannane with C_2F_5I.[4] In 1968 *Kawakami* an *Kuivila* succeeded in generating LiC_2F_5 from MeLi and C_2F_5I an the subsequent transfer of the C_2F_5 unit onto allyl tin and lea compounds.[5] The generation of LiC_2F_5 and its reaction wit organotin halides was improved by *Falck et al.* reaching yields u to 88 %.[6] Reacting donor stabilized bis(pentafluoroethyl) cadmium, $Cd(C_2F_5)_2{\cdot}D$, with trifluoroacetato- or nitratotrimethy stannane furnished $(C_2F_5)SnMe_3$ in moderate yields.[7] Althoug *Mehrabani et al.* employed AgC_2F_5 or $(C_2F_5)SiMe_3$ as transfe reagents, only small amounts of (pentafluoroethyl)tin halides wer formed. No attempts of optimization or isolation of these product were made.[8] LiC_2F_5 was also generated from C_2F_5H and *n*-BuLi i diethyl ether at −78 °C (Scheme 2). At temperatures above −40 ° decomposition of this compound to C_2F_4 und LiF was observed.[9



$$n\text{-BuLi} + C_2F_5H \xrightarrow[-\,C_4H_{10}]{-78\,^\circ C,\ Et_2O} LiC_2F_5 \xrightarrow{>-40\,^\circ C,\ Et_2O} LiF + C_2F$$

Scheme 2. Synthesis and decomposition of pentafluoroethyllithium, LiC_2F_5.

Herein, we report on the selective synthesis of (pentafluoroethyl)phenylstannanes, $(C_2F_5)_{4-n}SnPh_n$ (n = 1-3), by the reaction of LiC_2F_5 with the corresponding chlorophenyl-stannanes, $Cl_{4-n}SnPh_n$. The cleavage of the Sn-Ph bond with gaseous hydrogen halides HX (X = Cl, Br) leads to the corresponding (pentafluoroethyl)tin halides, $(C_2F_5)_{4-n}SnX_n$ (n = 1-3).

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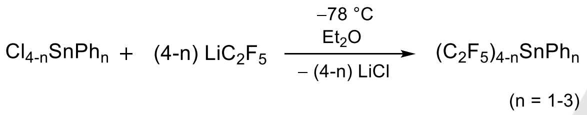
10.1002/chem.201701270

These species form adducts [$(C_2F_5)_{4-n}SnX_n$(phen)] (X = Br, n = 1-3; X = Cl, n = 1-2) with the chelating ligand 1,10-phenanthroline (phen).

Results and Discussion

The employment of LiC_2F_5 as a transfer reagent of the pentafluoroethyl group requires temperatures below −40 °C. Pentafluoroethyllithium was prepared in situ at −78 °C by the combination of *n*-BuLi with pentafluoroethane in a diethyl ether solution. The addition of $SnCl_4$ to this mixture results in the precipitation of a colorless solid, which presumably is the diethyl ether adduct of the Lewis acidic $SnCl_4$. Under these conditions, no selective reaction could be achieved, but this reaction is still under investigation in our laboratory. As expected, the substitution of one chlorine atom by a phenyl group leads to a decreased Lewis acidity. In keeping with this, no insoluble diethyl ether adduct of Cl_3SnPh was formed and the reaction of Cl_3SnPh with 3.5 equivalents of LiC_2F_5 selectively afforded tris(pentafluoroethyl)phenylstannane, $(C_2F_5)_3SnPh$. The product was isolated by distillation and obtained as a colorless liquid in an 83 % yield (Scheme 3).



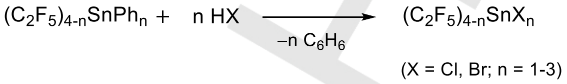
$$Cl_{4-n}SnPh_n + (4\text{-}n)\ LiC_2F_5 \xrightarrow[-\ (4\text{-}n)\ LiCl]{-78\ °C,\ Et_2O} (C_2F_5)_{4-n}SnPh_n \quad (n = 1\text{-}3)$$

Scheme 3. Synthesis of (pentafluoroethyl)phenylstannanes, $(C_2F_5)_{4-n}SnPh_n$ (n = 1-3).

Bis(pentafluoroethyl)diphenylstannane, $(C_2F_5)_2SnPh_2$, and (pentafluoroethyl)triphenylstannane, $(C_2F_5)SnPh_3$, were synthesized analogously from LiC_2F_5 and Cl_2SnPh_2 and $ClSnPh_3$, respectively. The employed protocol is also applicable for the synthesis of methyl substituted stannanes. Accordingly, dimethylbis(pentafluoroethyl)stannane, $(C_2F_5)_2SnMe_2$, was prepared in an 86 % yield as a colorless liquid with a vapor pressure of 15 mbar at 20 °C.

In order to obtain functionalized perfluoroalkylstannanes, the phenyl group had to be replaced by halogen atoms. Generally, the tin carbon bond of (perfluoroalkyl)organylstannane derivatives can be cleaved under relatively mild conditions by the use of elemental halogens X_2 or hydrogen halides HX.[6] *Jahn et al*. reported the quantitative conversion of $(CF_3)_3SnPh$ with elemental bromine at −15 °C.[2] Interestingly here, however, the addition of a large excess of bromine to a solution of $(C_2F_5)_3SnPh$ in chloroform did not lead to any observable reaction at room temperature even after a prolonged reaction time. This difference in reactivity can possibly be explained by the kinetic stabilization of the tin carbon bond provided by the increased steric hindrance of the pentafluoroethyl groups. A similar effect was described for $P(CF_3)_3$ and $P(C_2F_5)_3$. Tolman determined a cone angle of 137° for the $P(CF_3)_3$ ligand,[10] while the $P(C_2F_5)_3$ molecule exhibits a cone angle of 193° in the solid state and of 191° in the gas phase.[11]

By the reaction of $(C_2F_5)_3SnPh$ with gaseous hydrogen bromide at 130 °C, the desired bromostannane $(C_2F_5)_3SnBr$ was prepared in an 88 % yield as a colorless liquid and a vapor pressure of 15 mbar at 23 °C (Scheme 4).

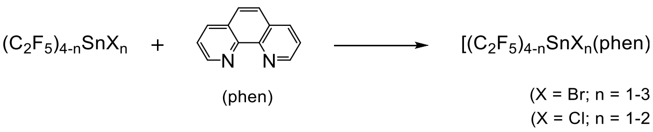


$$(C_2F_5)_{4-n}SnPh_n + n\ HX \xrightarrow[-n\ C_6H_6]{} (C_2F_5)_{4-n}SnX_n \quad (X = Cl, Br; n = 1\text{-}3)$$

Scheme 4. Synthesis of (pentafluoroethyl)tin halides, $(C_2F_5)_{4-n}SnX_n$ (X = Cl, Br; n = 1-3).

Analogously, the corresponding chlorostannane $(C_2F_5)_3SnC$ was obtained by the conversion of the phenylstannan $(C_2F_5)_3SnPh$ with hydrogen chloride at 170 °C in an 82 % yield a a colorless liquid and a slightly higher vapor pressure of 25 mba at 23 °C. The tin carbon bonds to the aryl groups i bis(pentafluoroethyl)diphenylstannane, $(C_2F_5)_2SnPh_2$, are shielde by only two C_2F_5 groups. Therefore the temperature of the reactio with HBr was reduced to 100 °C and $(C_2F_5)_2SnBr_2$ was isolated i an 84 % yield. A vapor pressure of 20 mbar of the colorless liqui was measured at 23 °C. $(C_2F_5)_2SnCl_2$ and $(C_2F_5)SnBr_3$ were als accessible via the solvent free reaction of the correspondin phenylstannanes with the HCl and HBr, respectively.

In order to obtain structural parameters of the nove (pentafluoroethyl)tin halides the compounds were converted int their 1,10-phenanthroline (phen) adducts. Adduct formation c (trifluoromethyl)tin halides, $(CF_3)_{4-n}SnX_n$ (X = F, Cl, Br; n = 1-3 with 1,10-phenanthroline was previously reported by *Eujen* an *Thurmann*.[1,12] Similarly, octahedrally configurated adducts of th (pentafluoroethyl)tin halides $(C_2F_5)_3SnBr$, $(C_2F_5)_3SnC$ $(C_2F_5)_2SnBr_2$, $(C_2F_5)_2SnCl_2$ and $(C_2F_5)SnBr_3$ were synthesized b the reaction with 1,10-phenanthroline in dichloromethane c acetonitrile solution (Scheme 5). Recrystallization of the product from dichloromethane or acetonitrile provided single crystal suitable for X-ray structure analyses. The formation of th 1,10-phenathroline adducts of the Lewis acidic stannanes thu constitutes a useful method for the identification of Lewis acidi stannanes.



Scheme 5. Synthesis of 1,10-phenanthroline adducts of (pentafluoroethyl)ti halides, [$(C_2F_5)_{4-n}SnX_n$(phen)] (X = Br, n = 1-3; X = Cl, n = 1-2).

The compounds [$(C_2F_5)_3SnBr$(phen)], [$(C_2F_5)_3SnCl$(phen)] and [$(C_2F_5)SnBr_3$(phen)] crystallize in the monoclinic space group *P*2$_1$/*n* and the compounds [$(C_2F_5)_2SnBr_2$(phen)] and [$(C_2F_5)_2SnCl_2$(phen)] crystallize in the orthorhombic space group *Pbca*. The molecular structures are shown in Figure 1. Selected bond lengths are given in Table 1 and crystal data and refinement characteristics are given in Table 3.

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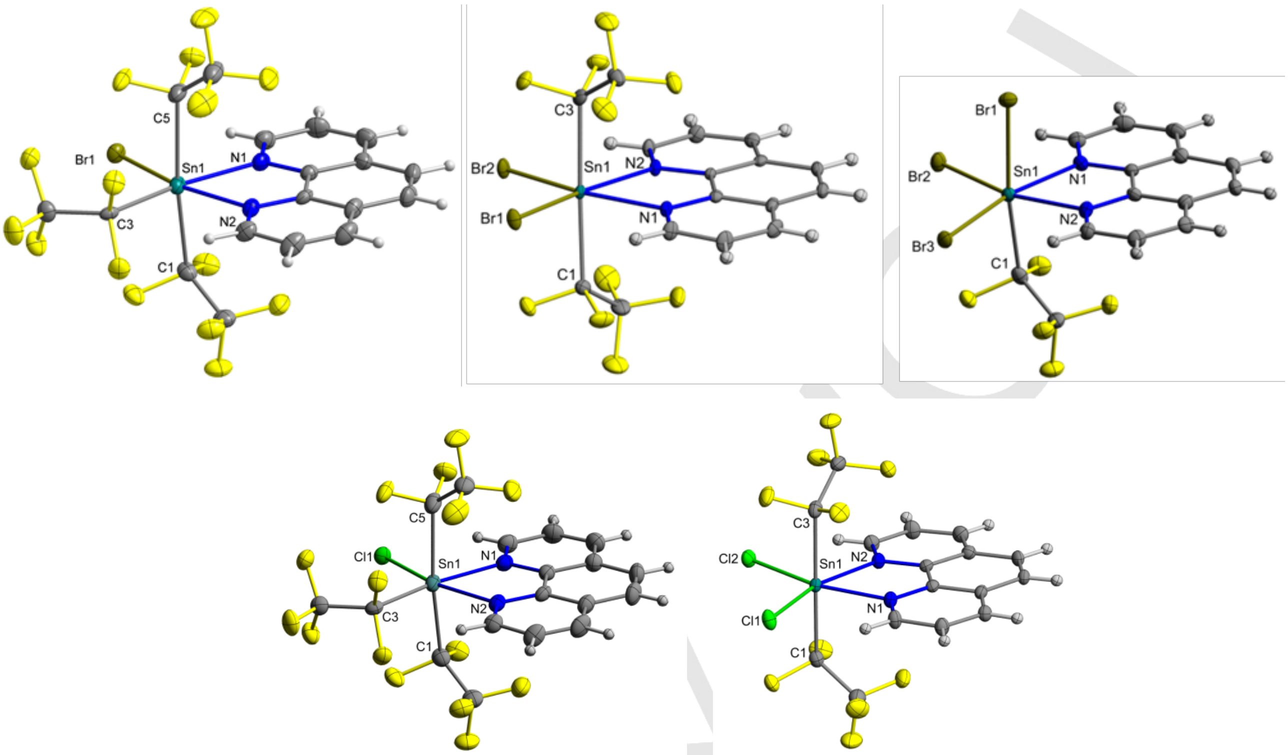
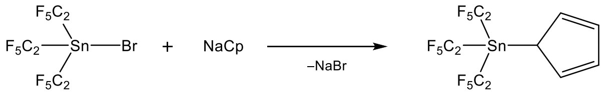


Figure 1. Molecular structures of the 1,10-phenanthroline adducts of bromo(pentafluoroethyl)stannanes (top) [$(C_2F_5)_3SnBr(phen)$] (left), [$(C_2F_5)_2SnBr_2(phen)$] (middle) and [$(C_2F_5)SnBr_3(phen)$] (right), and of the 1,10-phenanthroline adducts of chloro(pentafluoroethyl)stannanes (bottom) [$(C_2F_5)_3SnCl(phen)$] (left), [$(C_2F_5)_2SnCl_2(phen)$] (right); 50 % probability amplitude displacement ellipsoids are shown; selected bond lengths [pm] are given in Table 1.

In the series of [$(C_2F_5)_3SnBr(phen)$], [$(C_2F_5)_2SnBr_2(phen)$], [$(C_2F_5)SnBr_3(phen)$] (Figure 1) and [$SnBr_4(phen)$][13] an increasing number of bromine atoms is accompanied by a not very significant shortening of the Sn-N distance from 231 pm for [$(C_2F_5)_3SnBr(phen)$] to 226 pm for [$SnBr_4(phen)$]. The same tendency is observed for the corresponding chloro derivatives. These observations lead to the conclusion that the substitution of a bromine or a chlorine atom by the pentafluoroethyl group reduces the Lewis acidity of the resulting stannane. As expected the Sn-N bond of [$Me_2SnCl_2(phen)$][15] is elongated significantly by approximately 11 pm in comparison to [$(C_2F_5)_2SnCl_2(phen)$] which is due to an increased Lewis acidity in the perfluoroalkyl derivatives compared to the non-fluorinated alkylstannanes.

The (pentafluoroethyl)tin halides $(C_2F_5)_{4-n}SnX_n$ (X = Cl, Br) are useful starting materials for the synthesis of a wide variety of (pentafluoroethyl)stannane derivatives. The solvent free conversion of $(C_2F_5)_3SnBr$ with sodium cyclopentadienide at ambient temperature selectively afforded (η^1-cyclopentadienyl)-tris(pentafluoroethyl)stannane, $(C_2F_5)_3SnCp$, which was isolated in a 76 % yield (Scheme 6).



Scheme 6. Synthesis of (η^1-cyclopentadienyl)tris(pentafluoroethyl)stannane, $(C_2F_5)_3SnCp$.

Table 1. Selected bond lengths of 1,10-phenanthroline adducts of (pentafluoroethyl)tin halides [$(C_2F_5)_{4-n}SnX_n(phen)$] (X = Br, n = 1-3; X = Cl, n = 1-2) and literatu known stannanes [pm].

	$(C_2F_5)_3SnBr$ (**10**)	$(C_2F_5)_2SnBr_2$ (**12**)	$(C_2F_5)SnBr_3$ (**14**)	$SnBr_4$[13]	$(C_2F_5)_3SnCl$ (**11**)	$(C_2F_5)_2SnCl_2$ (**13**)	$SnCl_4$[14]	Me_2SnCl_2[15]
Sn-N(av)	231	230	227	226	230	228	224	239
Sn-X	257.73(6)	256(av)	255(av)	255(av)	244.59(13)	240(av)	237(av)	252(av)
Sn-C	228(av)	226(av)	226.8(4)	-	227(av)	225(av)	-	208(av)

For a structural characterization a crystal suitable for X ray diffraction was grown by crystallization of the liquid inside a sealed capillary in situ generating manually a crystal seed just under the melting temperature at -47 °C and subsequently slowly chilling down to -183 °C. $(C_2F_5)_3SnCp$ crystallizes in the monoclinic space group $P2_1/n$ and the molecular structure in the solid state confirms a η^1-coordination of the ring (Figure 2). Due to a fast sigmatropic rearrangement, the ^1H NMR spectrum of $(C_2F_5)_3SnCp$ shows only one singlet at 6.4 ppm with a $^2J(^1H,^{117/119}Sn)$ coupling constant of 34 Hz. The average C-Sn-C angle of the C_2F_5 groups (C1, C3, C5) of 103° is significantly smaller than the average C-Sn-C angle between the Cp carbon atom (C7) and the C_2F_5 groups (116°).

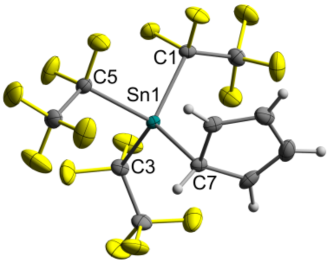


Figure 2. Molecular structure of $(C_2F_5)_3SnCp$; 50 % probability amplitude displacement ellipsoids are shown; selected bond lengths [pm] and angles [°]: Sn1-C1 220.4(2), Sn1-C3 221.7(2), Sn1-C5 221.2(2), Sn1-C7 214.8(2); C1-Sn1-C3 106.86(7), C1-Sn1-C5 97.72(7), C5-Sn1-C3 103.28(8), C7-Sn1-C1 117.81(7), C7-Sn1-C3 116.39(7), C7-Sn1-C5 112.32(8).

The ^{19}F NMR spectra of the tetracoordinated mono-, bis- and tris(pentafluoroethyl)stannanes exhibit two separate resonances for the CF_3 and the CF_2 units. The ^{19}F resonances of the hexacoordinated 1,10-phenanthroline adducts $[(C_2F_5)_3SnBr(phen)]$ and $[(C_2F_5)_3SnCl(phen)]$ show a spectrum of higher order with two sets of signals for the C_2F_5 groups in the ratio of 2:1. In general, the resonances of the CF_3 (−79.9 to −86.7 ppm) and the CF_2 groups (−108.7 to −123.0 ppm) lie in a narrow range and apparently are not depending on the substitution pattern at the Sn center. However, the $^2J(^{119}Sn,^{19}F)$ coupling constants of the fluorine atoms of the CF_2 groups of the tetracoordinated stannanes are sensitive towards the electronic character of the substituents. Whereas higher values are observed for stannanes bearing electron withdrawing groups like $(C_2F_5)SnBr_3$ or $(C_2F_5)_2SnCl_2$, smaller constants are observed for electron rich substituted stannanes such as $(C_2F_5)SnPh_3$ and $(C_2F_5)_2SnMe_2$ (see Table 2). A similar trend is observed for the $^1J(^{119}Sn,^{13}C)$ and $^2J(^{119}Sn,^{13}C)$ coupling constants. $(C_2F_5)SnBr_3$ shows significant larger coupling constants than $(C_2F_5)SnPh_3$ (see Table 2). The $^2J(^{119}Sn,^{19}F)$ and the $^1J(^{119}Sn,^{13}C)$ coupling constants are strongly correlated. The correlation is depicted in Figure 3 with a coefficient of determination of 0.992. A similar correlation was observed by *Eujen* and *Thurmann* for (trifluoromethyl)stannanes. Furthermore they determined the signs of the $^2J(^{119}Sn,^{19}F)$ and $^1J(^{119}Sn,^{13}C)$ coupling constants which are both negative[16].

Table 2. $^1J(^{119}Sn,^{13}C)$, $^2J(^{119}Sn,^{13}C)$ and $^2J(^{119}Sn,^{19}F)$ coupling constants of pentafluoroethyl groups of stannanes.

	$^1J(^{119}Sn,^{13}C)$/Hz	$^2J(^{119}Sn,^{13}C)$/Hz	$^2J(^{119}Sn,^{19}F)$/Hz
$(C_2F_5)SnPh_3$	-394	55	-237
$(C_2F_5)_2SnMe_2$	-423	62	-264
$(C_2F_5)_2SnPh_2$	-472	67	-273
$(C_2F_5)_3SnCp$	-504	85	-324
$(C_2F_5)_3SnPh$	-551	81	-323
$(C_2F_5)_3SnBr$	-747	112	-450
$(C_2F_5)_3SnCl$	-760	113	-460
$(C_2F_5)_2SnBr_2$	-883	134	-525
$(C_2F_5)_2SnCl_2$	-973	140	-553
$(C_2F_5)SnBr_3$	-1113	165	-625

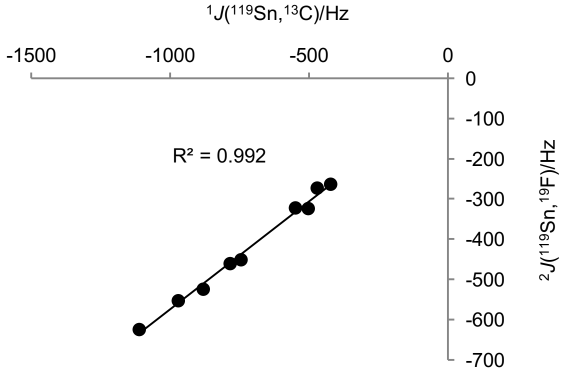


Figure 3. Correlation of $^1J(^{119}Sn,^{13}C)$ and $^2J(^{119}Sn,^{19}F)$ coupling constants of (pentafluoroethyl)stannanes.

For the C_2F_5 derivatives the signs of the $^2J(^{119}Sn,^{19}F)$ and the $^1J(^{119}Sn,^{13}C)$ coupling constants were determined by $^{19}F,^{13}C$ and $^{19}F,^{119}Sn$ 2D NMR experiments. Figure 4 shows the $^{19}F,^{13}C$ HMQC (left) and $^{19}F,^{119}Sn$ HMQC (right) 2D NMR correlation spectrum of $(C_2F_5)_2SnBr_2$. The values for the $^1J(C,F)$ coupling constant as well as for the reduced coupling constant $^1K(C,F)$ are defined as negative ($^1J(C,F) < 0$).[17] The $^{19}F,^{119}Sn$ HMQC spectrum (right) shows a negative slope for the line between the ^{13}C satellites. In consequence, the reduced coupling constants $^1K(C,F)$ and $^1K(C,Sn)$ (> 0) have opposite signs. By the conversion to the $^1J(^{13}C,^{119}Sn)$ coupling constant[17],

$$^1J(\mathrm{C,Sn}) = \frac{h\,\gamma_{\mathrm{Sn}}\,\gamma_{\mathrm{C}}}{4\,\pi^2}\;{}^1K(\mathrm{C,Sn})$$

a negative sign ($^1J(^{13}C,^{119}Sn) < 0$) is determined due to the negative gyromagnetic ratio of tin and the positive gyromagnetic ratio of carbon ($\gamma_{Sn} < 0$, $\gamma_C > 0$). Taking into account that the $^1J(^{13}C,^{119}Sn)$ coupling constant of (pentafluoroethyl)stannanes is negative the sign of the $^2J(^{119}\mathrm{Sn},^{19}\mathrm{F})$ can be determined by the $^{19}\mathrm{F},^{13}\mathrm{C}$ HMQC spectrum (Figure 4 left). The tin satellites in this spectrum show a positive slope, thus the reduced coupling constants $^1K(\mathrm{C,Sn})$ and $^2K(\mathrm{Sn,F})$ exhibit the same sign (both > 0). Hence, by the conversion to the $^2J(^{119}\mathrm{Sn},^{19}\mathrm{F})$ coupling constant,

$$^2J(\mathrm{Sn,F}) = \frac{h\,\gamma_{\mathrm{Sn}}\,\gamma_{\mathrm{F}}}{4\,\pi^2}\;^2K(\mathrm{Sn,F})$$

again a negative sign ($^2J(^{119}\mathrm{Sn},^{19}\mathrm{F}) < 0$) is determined due to the negative gyromagnetic ratio of tin ($\gamma_{\mathrm{Sn}} < 0$) and the positive ratio of fluorine ($\gamma_{\mathrm{F}} > 0$). Consequently, the signs of the $^1J(^{13}\mathrm{C},^{119}\mathrm{Sn})$ and the $^2J(^{119}\mathrm{Sn},^{19}\mathrm{F})$ coupling constants of the (pentafluoroethyl)stannanes as well as of the (trifluoromethyl)stannanes are negative.[16]

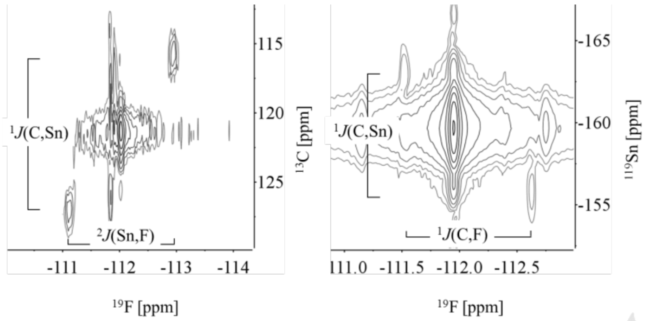


Figure 4. Details of the $^{19}\mathrm{F},^{13}\mathrm{C}$ HMQC (left) and $^{19}\mathrm{F},^{119}\mathrm{Sn}$ HMQC (right) 2D NMR correlation spectra of neat $(\mathrm{C_2F_5})_2\mathrm{SnBr_2}$ for the determination of the sign of the coupling constants.

The $^{119}\mathrm{Sn}$ NMR spectra of tetracoordinated stannanes reveal resonances from −33 to −335 ppm whereas the $^{119}\mathrm{Sn}$ nuclei in the hexacoordinated phenanthroline adducts are more shielded (−475 to −857 ppm).

In general, multinuclear NMR spectroscopy is an excellent tool for the characterization of (pentafluoroethyl)stannanes. Dimethylbis(pentafluoroethyl)stannane, $(\mathrm{C_2F_5})_2\mathrm{SnMe_2}$, could be fully characterized by NMR spectroscopy because all elements in this molecule have at least one isotope with a nuclear spin of I = ½ and are therefore observable by NMR spectroscopy. The $^1\mathrm{H}$ NMR spectrum is characterized by a singlet at 0.74 ppm with tin satellites ($^2J(^1\mathrm{H},^{117/119}\mathrm{Sn})$ = 62 Hz) demonstrating the bonding to the tin atom. Two singlets are observed in the $^{19}\mathrm{F}$ NMR spectrum at −83.3 ppm for the $\mathrm{CF_3}$ unit and at −118.2 ppm for the $\mathrm{CF_2}$ unit with a $^2J(^{19}\mathrm{F},^{117/119}\mathrm{Sn})$ coupling constant of 251/264 Hz.

The respective number of methyl and pentafluoroethyl substituents is determined by the multiplicity in the $^{119}\mathrm{Sn}$ NMR spectrum. The $^{119}\mathrm{Sn}\{^{19}\mathrm{F}\}$ NMR spectrum reveals a septet at −33.2 ppm with a $^2J(^{119}\mathrm{Sn},^1\mathrm{H})$ coupling constant of 63 Hz due to the coupling to six hydrogen atoms (see Figure 5 top). The $^{119}\mathrm{Sn}\{^1\mathrm{H}\}$ NMR shows a quintet of septets due to the coupling to four fluorine atoms of two $\mathrm{CF_2}$ units ($^2J(^{119}\mathrm{Sn},^{19}\mathrm{F})$ = 263 Hz) and to the six fluorine atoms of two $\mathrm{CF_3}$ units ($^3J(^{119}\mathrm{Sn},^{19}\mathrm{F})$ = 3 Hz) (see Figure 5 middle). Consequently, the non-decoupled $^{119}\mathrm{Sn}$ NMR spectrum reveals a quintet of septets of septets (see Figure 5 bottom). In the $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR spectrum the methyl groups give rise to a singlet at −9.9 ppm with tin satellites of $^1J(^{13}\mathrm{C},^{117/119}\mathrm{Sn})$ = 367/385 Hz. The $^{13}\mathrm{C}\{^{19}\mathrm{F}\}$ NMR shows a singlet at 120.2 ppm ($^2J(^{13}\mathrm{C},^{117/119}\mathrm{Sn})$ = 60/62 Hz) for the $\mathrm{CF_3}$ units and a septet at 124.2 ppm ($^1J(^{13}\mathrm{C},^{117/119}\mathrm{Sn})$ = 404/423 Hz) for the $\mathrm{CF_2}$ units with tin satellites. The sepet is caused by the long range $^3J(^{13}\mathrm{C},^1\mathrm{H})$ coupling of 2 Hz to the methyl groups.

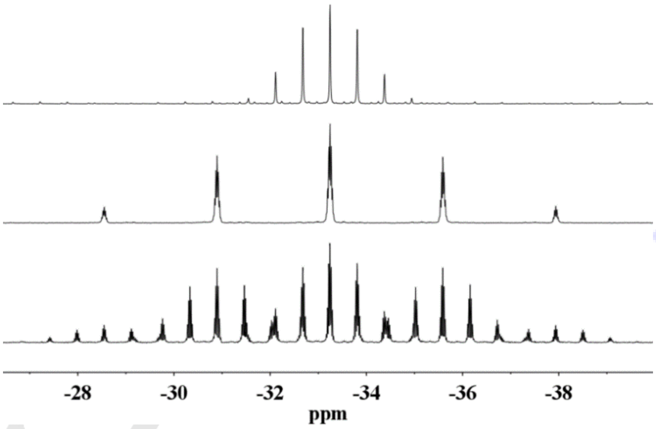


Figure 5. $^{119}\mathrm{Sn}\{^{19}\mathrm{F}\}$ (top), $^{119}\mathrm{Sn}\{^1\mathrm{H}\}$ (middle) and $^{119}\mathrm{Sn}$ (bottom) NMR spectra of $(\mathrm{C_2F_5})_2\mathrm{SnMe_2}$.

Conclusions

$\mathrm{LiC_2F_5}$ is an excellent transfer reagent for the introduction of pentafluoroethyl groups in to chlorophenylstannanes, $\mathrm{Cl_nSnPh_{4-n}}$, to obtain (pentafluoroethyl)phenylstannanes, $(\mathrm{C_2F_5})_{4-n}\mathrm{SnPh_n}$ (n = 1-3), in good yields of 83 - 91 %.

These phenylstannanes react with gaseous hydrogen halides HX (X = Cl, Br) to the corresponding (pentafluoroethyl)tin halides, $(\mathrm{C_2F_5})_{4-n}\mathrm{SnX_n}$ (n = 1-3), in yields of 72 - 88 %. The reaction of these organotin halides with the chelating ligand 1,10-phenanthroline (phen) results in the complexes $[(\mathrm{C_2F_5})_{4-n}\mathrm{SnX_n(phen)}]$, which were characterized by single crystal X-ray diffraction. The structural parameters reflect an increased Lewis acidity of the (pentafluoroethyl)tin halides compared to non-fluorinated derivatives. For the synthesis of methyl(pentafluoroethyl)stannanes the same procedure is applied The composition of $(\mathrm{C_2F_5})_2\mathrm{SnMe_2}$ was completely deduced by means of NMR spectroscopy. The (pentafluoroethyl)tin halides are suited for further functionalization as for example shown by the reaction with sodium cyclopentadienide yielding the corresponding (η^1-cyclopentadienyl)tris(pentafluoroethyl)-stannane $(\mathrm{C_2F_5})_2\mathrm{SnCp}$.

The development of an efficient protocol for the synthesis of (pentafluoroethyl)stannanes opens the door to a rich area of tin chemistry which is currently under investigation in our laboratory.

Experimental Section

All chemicals were obtained from commercial sources and used without further purification. Standard high vacuum techniques were employed throughout all preparative procedures. Gas pressures in the range from atmospheric pressure to 1 mbar were measured with the vacuubrand DVR 2, a piezo vacuum gauge. Nonvolatile compounds were handled in a dry N_2 atmosphere using Schlenk techniques.. The NMR spectra were recorded on a Bruker Model Avance III 300 spectrometer (^{1}H 300.13 MHz, ^{13}C 75.47 MHz, ^{19}F 282.40 MHz, ^{119}Sn 111.9 MHz) with positive shifts being downfield from the external standards (TMS (^{1}H, ^{13}C), CCl_3F (^{19}F), and $SnMe_4$ (^{119}Sn)). The NMR spectra were recorded in the indicated deuterated solvent or in relation to [D$_6$]acetone filled capillaries. IR spectra were recorded on an ALPHA-FT-IR spectrometer (Bruker). EI mass spectra were recorded using an Autospec X magnetic sector mass spectrometer with EBE geometry (Vacuum Generators, Manchester, UK) equipped with a standard EI or CI source. Samples were introduced by push rod in aluminium crucibles or by direct gas phase injection. Ions were accelerated by 8 kV in EI mode. The crystal data were collected using graphite-monochromated Mo-K$_\alpha$ radiation (λ = 71.073 pm). The structures were solved by Direct Methods and refined by full-matrix least-squares cycles using SHELXS-97 and SHELXL-97 [18]. CCDC-1003536 (**10**), CCDC-1003537(**11**), CCDC-1003538 (**12**), CCDC-1003539 (**13**), CCDC-1003540 (**14**) and CCDC-1003541 (**15**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Tris(pentafluoroethyl)phenylstannane (1): An *n*-butyllithium/*n*-hexane solution (70 mL, c = 1.6 mol · L^{-1}, 112 mmol) was diluted with 300 mL of diethyl ether, cooled to -78 °C, degassed and stirred under an atmosphere of pentafluoroethane (125 mmol) for 20 min. Trichlorophenylstannane (9.69 g, 32.1 mmol) was added and the reaction mixture was allowed to warm to ambient temperature (3 h). The resulting suspension was filtered and all volatile compounds were removed from the filtrate under reduced pressure. The obtained crude product (16.1 g) was purified by vacuum distillation ($1\cdot10^{-6}$ bar, b.p.: 32 °C). $(C_2F_5)_3SnPh$ was obtained as a colorless liquid (14.8 g, 26.8 mmol, 83 %). ^{1}H NMR ([D]chloroform, 298 K): δ=7.5-7.7 ppm (m; Ph); ^{13}C{^{1}H} NMR ([D]chloroform, 298 K): δ=127.3 (s; *ipso*-C), 130.2 (s, *J*(C,Sn)=71/74 Hz; arom. C), 132.5 (s, *J*(C,Sn)=16 Hz; arom. C), 136.1 ppm (s, *J*(C,Sn)=49 Hz; arom. C); ^{13}C{^{19}F} NMR ([D]chloroform, 298 K): δ=119.4 (s, ^{2}J(C,Sn)=77/81 Hz; CF_3), 125.8 ppm (s, ^{1}J(C,Sn)=527/551 Hz; CF_2); ^{19}F NMR ([D]chloroform, 298 K): δ=-110.5 (s, ^{2}J(F,Sn)=310/323 Hz; CF_2), -82.9 ppm (s; CF_3); ^{119}Sn{^{1}H} NMR ([D]chloroform, 298 K): δ=-234.1 ppm (sept, m, ^{2}J(F,Sn)=324 Hz); MS (EI, 20 eV) {m/z (%) [assignment]}: 77.0 (95) $[C_6H_5]^+$, 100.0 (59) $[C_2F_4]^{\cdot+}$, 119.9 (19) $[Sn]^{\cdot+}$, 127.0 (36), 138.9 (67) $[SnF]^+$, 177.0 (38) $[PhC_2F_4]^+$, 196.9 (39) $[SnPh]^+$, 215.9 (7) $[SnPhF]^{\cdot+}$, 234.9 (100) $[SnPhF_2]^+$, 334.9 (48) $[(C_2F_5)SnPhF]^+$, 434.9 (25) $[(C_2F_5)_2SnPh]^+$; IR (ATR): $\tilde{\nu}$=3066 (w), 1540 (w), 1487 (w), 1436 (w), 1314 (s), 1294 (m), 1191 (s), 1084 (s), 1022 (w), 999 (w), 930 (s), 738 (m), 728 (m), 691 (m), 604 (w), 588 (w), 536 (w), 441 (m) cm^{-1}.

Bis(pentafluoroethyl)diphenylstannane (2): Pentafluoroethyllithium was generated as described for **(1)** from an *n*-butyllithium/*n*-hexane solution (49 mL, c = 1.6 mol · L^{-1}, 78 mmol) and pentafluoroethane (94 mmol) in 250 mL of diethyl ether. A solution of dichlorodiphenylstannane (11.3 g, 32.9 mmol) in diethyl ether (20 mL) was added and the reaction mixture was allowed to warm to ambient temperature (3 h). The resulting suspension was filtered and all volatile compounds were removed under reduced pressure. The obtained crude product (16.3 g) was purified by vacuum distillation ($1\cdot10^{-6}$ bar, b.p.: 65 °C). $(C_2F_5)_2SnPh_2$ was obtained as a colorless liquid (13.7 g, 26.8 mmol, 82 %). ^{1}H NMR ([D]chloroform, 298 K): δ=7.3-7.7 ppm (m; Ph); ^{13}C{^{1}H} NMR ([D]chloroform, 298 K): δ=129.8 (s, *J*(C,Sn)=64 Hz; arom. C), 130.1 (s; *ipso*-C), 131.5 (s, *J*(C,Sn)=14 Hz; arom. C), 136.8 ppm (s, *J*(C,Sn)=45 Hz; arom. C); ^{13}C{^{19}F} NMR ([D]chloroform, 298 K): δ=120.3 (s, ^{2}J(C,Sn)=65/67 Hz; CF_3), 126.3 ppm (s, ^{1}J(C,Sn)=450/472 Hz; CF_2); ^{19}F NMR ([D]chloroform, 298 K): δ=-113.8 (s, ^{2}J(F,Sn)=262/273 Hz; CF_2), -82.5 ppm (s; CF_3); ^{119}Sn{^{1}H} NMR ([D]chloroform, 298 K): δ=-186.1 ppm (quin, ^{2}J(F,Sn)=273 Hz); MS (EI, 20 eV) {m/z (%) [assignment]}: 77.0 (18) $[C_6H_5]^+$, 119.9 (5) $[Sn]^{\cdot+}$, 127.0 (31), 138.9 (13) $[SnF]^+$, 177.0 (15) $[PhC_2F_4]^+$, 196.9 (22) $[SnPh]^+$, 234.9 (9) $[SnPhF_2]^+$, 293.0 (100) $[SnPh_2F]^+$, 334.9 (5) $[(C_2F_5)SnPhF]^+$, 393.0 (38) $[(C_2F_5)SnPh_2]^+$, 434.9 (3) $[(C_2F_5)_2SnPh]^+$; IR (ATR): $\tilde{\nu}$=3076 (w), 1581 (w), 1487 (w), 1433 (w), 1314 (s), 1293 (m), 1188 (s), 1093 (s), 1070 (s), 1023 (w), 998 (w), 930 (s), 727 (s), 693 (s), 601 (w), 585 (w), 534 (w), 443 (m) cm^{-1}.

(Pentafluoroethyl)triphenylstannane (3): Pentafluoroethyllithium was generated as described for **(1)** from an *n*-butyllithium/*n*-hexane solution (55 mL, c = 1.6 mol · L^{-1}, 88 mmol) and pentafluoroethane (100 mmol) in 250 mL of diethyl ether. Chlorotriphenylstannane (30.5 g, 79.1 mmol), dissolved in diethyl ether (20 mL), was added and the reaction mixture was allowed to warm to ambient temperature (3 h). The resulting suspension was filtered, and the filter cake was washed twice with 100 mL of diethyl ether. All volatile compounds were removed under reduced pressure, the residue was dissolved in toluene and filtered again. After removing all volatile compounds under reduced pressure $(C_2F_5)SnPh_3$ was obtained as a colorless solid (33.9 g, 72.3 mmol, 91 %). ^{1}H NMR ([D]chloroform, 298 K): δ=7.5-7.8 ppm (m; Ph); ^{13}C{^{1}H} NMR ([D]chloroform, 298 K): δ=129.2 (s, *J*(C,Sn)=56/58 Hz; arom. C), 130.4 (s, *J*(C,Sn)=13 Hz; arom. C), 133.7 (t, ^{3}J(C,F)=2 Hz; *ipso*-C), 137.2 ppm (s, *J*(C,Sn)=40 Hz; arom. C); ^{13}C{^{19}F} NMR ([D]chloroform, 298 K): δ=120.9 (s, ^{2}J(C,Sn)=53/55 Hz; CF_3), 126.5 ppm (s, ^{1}J(C,Sn)=376/394 Hz; CF_2); ^{19}F NMR ([D]chloroform, 298 K): δ=-116.4 (t, ^{3}J(F,F)=1.9 Hz ^{2}J(F,Sn)=227/237 Hz; CF_2), -82.1 ppm (t, ^{3}J(F,F)=1.9 Hz; CF_3); ^{119}Sn{^{1}H} NMR ([D]chloroform, 298 K): δ=-149.7 ppm (t, m, ^{2}J(F,Sn)=238 Hz); MS (EI, 20 eV) {m/z (%) [assignment]}: 119.9 (7) $[Sn]^{\cdot+}$, 196.9 (19) $[SnPh]^+$, 293.0 (3) $[SnPh_2F]^+$, 351.0 (100) $[SnPh_3]^+$; IR (ATR): $\tilde{\nu}$=3071 (w), 2989 (w), 1581 (w), 1481 (m), 1430 (m), 1316 (s), 1292 (m), 1181 (s), 1089 (s), 1075 (s), 1048 (s), 1022 (m), 996 (m), 971 (w), 928 (s), 726 (s), 695 (s), 661 (m), 598 (w), 583 (w), 533 (w), 441(s) cm^{-1}.

Dimethylbis(pentafluoroethyl)stannane (4): Pentafluoroethyllithium was generated as described for **(1)** from an *n*-butyllithium/*n*-hexane solution (43 mL, c = 1.6 mol · L^{-1}, 69 mmol) and pentafluoroethane (75 mmol) in 200 mL of diethyl ether. Dichlorodimethylstannane (5.27 g, 24.0 mmol), dissolved in diethyl ether (150 mL), was added and the reaction mixture was allowed to warm to ambient temperature (3 h). The resulting slurry was filtered and the solvents were removed from the filtrate by an isotherm distillation at -60 °C. Fractional condensation yielded $(C_2F_5)_2SnMe_2$ in the -60 °C cold trap as a colorless liquid (7.69 g, 19.9 mmol, 83 %, vapor pressure 15 mbar at 23 °C). ^{1}H NMR ([D]chloroform, 298 K): δ=0.74 ppm (s, ^{2}J(H,Sn)=62 Hz; CH_3); ^{13}C{^{1}H} NMR ([D]chloroform, 298 K): δ=-9.9 ppm (s, ^{1}J(C,Sn)=367/385 Hz; CH_3); ^{13}C{^{19}F} NMR ([D]chloroform, 298 K): δ=120.2 (s, ^{2}J(C,Sn)=60/62 Hz; CF_3), 124.2 ppm (sept, ^{3}J(C,H)=2 Hz, ^{1}J(C,Sn)=404/423 Hz; CF_2); ^{19}F NMR ([D]chloroform, 298 K): δ =-118.8 (s, ^{2}J(F,Sn)=251/264 Hz; CF_2), -83.3 ppm (s; CF_3); ^{119}Sn{^{1}H} NMR ([D]chloroform, 298 K): δ=-33.2 ppm (quin, sept, ^{2}J(Sn,F)=263 Hz, ^{3}J(Sn,F)=3 Hz); ^{119}Sn{^{19}F} NMR ([D]chloroform, 298 K): δ=-33.2 ppm (sept, ^{2}J(Sn,H)=63 Hz); ^{119}Sn NMR ([D]chloroform, 298 K): δ =-33.2 ppm (quin, sept, sept, ^{2}J(Sn,F)=263 Hz, ^{2}J(Sn,H)=63 Hz, ^{3}J(Sn,F)=3 Hz); MS (EI, 20 eV) {m/z (%) [assignment]}: 69.0 (12), 100.0 (5) $[C_2F_4]^{\cdot+}$, 119.9 (9) $[Sn]^{\cdot+}$, 134.9 (26) $[SnCH_3]^+$, 168.9 (100) $[Sn(CH_3)_2F]^+$, 172.9 (41) $[SnCH_3F_2]^+$, 268.9 (13) $[(C_2F_5)Sn(CH_3)_2]^+$, 272.9 (11) $[(C_2F_5)SnCH_3F]^+$; IR (gas phase): $\tilde{\nu}$=3011 (w), 2931 (w), 1538 (w), 1415 (w), 1323 (s), 1299 (m),

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1218 (s), 1202 (s), 1117 (s), 1087 (m), 1074 (m), 941 (m), 778 (w), 738 (m), 600 (w), 552 (w), 528 (w) cm^{-1}.

Bromotris(pentafluoroethyl)stannane (5): Tris(pentafluoroethyl)phenylstannane, $(C_2F_5)_3SnPh$, (10.3 g, 18.6 mmol) and gaseous hydrogen bromide (27.5 mmol) were loaded into a 500 mL ampoule with a Young valve and stirred for 16 h at 130 °C. A fractional condensation yielded the crude product in a -80 °C cooled trap contaminated with benzene. Benzene was removed by an isothermal distillation to give the bromostannane $(C_2F_5)_3SnBr$ as a colorless liquid with a vapor pressure of 15 mbar at 23 °C (9.1 g, 16.4 mmol, 88 %). $^{13}C\{^{19}F\}$ NMR ([D]chloroform, 298 K): δ=118.8 (s, ^{2}J(C,Sn)=107/112 Hz; CF_3), 123.9 ppm (s, ^{1}J(C,Sn)=714/747 Hz; CF_2); ^{19}F NMR ([D]chloroform, 298 K): δ=-108.7 (s, ^{2}J(F,Sn)=430/450 Hz; CF_2), -81.7 ppm (s; CF_3); ^{119}Sn NMR ([D]chloroform, 298 K): δ=-240.0 ppm (sept, ^{2}J(Sn,F=451 Hz); MS (EI, 20 eV) {m/z (%) [assignment]}: 100.0 (82) $[C_2F_4]^{\cdot +}$, 119.0 (17) $[C_2F_5]^+$, 119.9 (3) $[Sn]^{\cdot +}$, 138.9 (27) $[SnF]^+$, 198.8 (42) $[SnBr]^+$, 336.8 (100) $[(C_2F_5)SnBrF]^+$, 376.9 (5) $[(C_2F_5)_2SnF]^+$, 436.8 (24) $[(C_2F_5)_2SnBr]^+$; IR (gas phase): $\tilde{\nu}$=1320 (s), 1299 (m), 1228 (s), 1119 (s), 939 (s), 742 (m) cm^{-1}.

Chlorotris(pentafluoroethyl)stannane (6): Analogously to the protocol for **(5),** tris(pentafluoroethyl)phenylstannane, $(C_2F_5)_3SnPh$, (14.4 g, 26.0 mmol) and gaseous hydrogen chloride (35.0 mmol) were combined at 170 °C for 72 h to afford the chlorostannane $(C_2F_5)_3SnCl$ as a colorless liquid with a vapor pressure of 25 mbar at 23 °C (10.9 g, 21.3 mmol, 82 %). $^{13}C\{^{19}F\}$ NMR ([D]chloroform, 298 K): δ=118.6 (s, ^{2}J(C,Sn)=108/113 Hz; CF_3), 125.2 ppm (s, ^{1}J(C,Sn)=727/760 Hz; CF_2); ^{19}F NMR ([D]chloroform, 298 K): δ=-108.7 (s, ^{2}J(F,Sn)=441/460 Hz; CF_2), -82.0 ppm (s; CF_3); ^{119}Sn NMR ([D]chloroform, 298 K): δ=-206.9 ppm (sept, ^{2}J(Sn,F)=462 Hz); MS (EI, 20 eV) {m/z (%) [assignment]}: 100.0 (100) $[C_2F_4]^{\cdot +}$, 119.0 (17) $[C_2F_5]^+$, 119.9 (3) $[Sn]^{\cdot +}$, 138.9 (26) $[SnF]^+$, 154.9 (33) $[SnCl]^+$, 276.9 (5) $[(C_2F_5)SnF_2]^+$, 292.9 (43) $[(C_2F_5)SnClF]^+$, 376.9 (10) $[(C_2F_5)_2SnF]^+$, 392.9 (10) $[(C_2F_5)_2SnCl]^+$; IR (gas phase): $\tilde{\nu}$=1320 (s), 1299 (m), 1230 (s), 1120 (s), 940 (s), 742 (m) cm^{-1}.

Dibromobis(pentafluoroethyl)stannane (7): Analogously to the protocol for **(5)** bis(pentafluoroethyl)diphenylstannane, $(C_2F_5)_2SnPh_2$, (26.5 g, 51.9 mmol) and gaseous hydrogen bromide (120 mmol) were reacted at 100 °C for 16 h to yield the bromostannane $(C_2F_5)_2SnBr_2$ as a colorless liquid with a vapor pressure of 20 mbar at 23 °C (23.1 g, 44.7 mmol, 86 %). $^{13}C\{^{19}F\}$ NMR ([D]chloroform, 298 K): δ=118.8 (s, ^{2}J(C,Sn)=128/134 Hz; CF_3), 122.0 ppm (s, ^{1}J(C,Sn)=843/883 Hz; CF_2); ^{19}F NMR ([D]chloroform, 298 K): δ=-110.0 (s, ^{2}J(F,Sn)=502/525 Hz; CF_2), -80.7 ppm (s; CF_3); ^{119}Sn NMR ([D]chloroform, 298 K): δ=-232.3 ppm (quin, ^{2}J(Sn,F)=524 Hz); MS (EI, 20 eV) {m/z (%) [assignment]}: 100.0 (89) $[C_2F_4]^{\cdot +}$, 119.0 (30) $[C_2F_5]^+$, 119.9 (10) $[Sn]^{\cdot +}$, 138.9 (30) $[SnF]^+$, 198.8 (40) $[SnBr]^+$, 277.7 (16) $[SnBr_2]^{\cdot +}$, 296.7 (92) $[SnBr_2F]^+$, 336.8 (8) $[(C_2F_5)SnBrF]^+$, 396.7 (100) $[(C_2F_5)SnBr_2]^+$; IR (gas phase): $\tilde{\nu}$=1320 (s), 1297 (m), 1226 (s), 1118 (s), 938 (s), 742 (m) cm^{-1}.

Dichlorobis(pentafluoroethyl)stannane (8): Analogously to the protocol for **(5)** bis(pentafluoroethyl)diphenylstannane, $(C_2F_5)_2SnPh_2$, (5.76 g, 11.3 mmol) and gaseous hydrogen chloride (26 mmol) reacted at 75 °C for 16 h to furnish the chlorostannane $(C_2F_5)_2SnCl_2$ as a colorless liquid with a vapor pressure of 50 mbar at 23 °C (3.48 g, 8.14 mmol, 72 %). $^{13}C\{^{19}F\}$ NMR ([D]chloroform, 298 K): δ=118.7 (s, ^{2}J(C,Sn)=134/140 Hz; CF_3), 124.8 ppm (s, ^{1}J(C,Sn)=931/973 Hz; CF_2); ^{19}F NMR ([D]chloroform, 298 K): δ=-109.8 (s, ^{2}J(F,Sn)=529/553 Hz; CF_2), -81.4 ppm (s; CF_3); ^{119}Sn NMR ([D]chloroform, 298 K): δ=-141.2 ppm (quin, ^{2}J(F,Sn)=554 Hz); MS (EI, 20 eV) {m/z (%) [assignment]}: 100.0 (100) $[C_2F_4]^{\cdot +}$, 119.0 (23) $[C_2F_5]^+$, 138.9 (10) $[SnF]^+$, 154.9 (22) $[SnCl]^+$, 208.8 (31) $[SnCl_2F]^+$, 292.9 (6) $[(C_2F_5)SnClF]^+$, 308.8 (20) $[(C_2F_5)SnCl_2]^+$; IR (gas phase): $\tilde{\nu}$=1322 (s), 1299 (m), 1227 (s), 1120 (s), 939 (s), 743 (m), 608 (w), 402 (m) cm^{-1}.

Tribromo(pentafluoroethyl)stannane (9): Analogously to the protocol for **(5)**, the reaction of (pentafluoroethyl)triphenylstannane, $(C_2F_5)SnPh_3$, (15.66 g, 33.39 mmol) and gaseous hydrogen bromide (105 mmol) at 100 °C for 36 h gave the bromostannane $(C_2F_5)SnBr_3$ as a colorless liquid with a vapor pressure of 7 mbar at 22 °C (11.9 g, 24.9 mmol, 75 %). $^{13}C\{^{19}F\}$ NMR ([D]chloroform, 298 K): δ=118.7 (s, ^{2}J(C,Sn)=157/165 Hz; CF_3), 119.1 ppm (s, ^{1}J(C,Sn)=1064/1113 Hz, CF_2); ^{19}F NMR ([D]chloroform, 298 K): δ=-111.3 (q, ^{3}J(F,F)=4 Hz, ^{2}J(F,Sn)=598/625 Hz; CF_2), -79.9 ppm (t, ^{3}J(F,F)=4 Hz, ^{3}J(F,Sn)=23 Hz; CF_3); ^{119}Sn NMR ([D]chloroform, 298 K): δ=-335.3 ppm (t, ^{2}J(F,Sn)=625 Hz); MS (EI, 20 eV) {m/z (%) [assignment]}: 69.0 (13), 78.0 (28), 100.0 (63) $[C_2F_4]^{\cdot +}$, 119.0 (12) $[C_2F_5]^+$, 119.9 (12) $[Sn]^{\cdot +}$, 138.9 (14) $[SnF]^+$, 198.8 (42) $[SnBr]^+$, 277.7 (9) $[SnBr_2]^{\cdot +}$, 296.7 (12) $[SnBr_2F]^+$, 314.7 (21), 358.7 (100) $[SnBr_3]^+$, 396.7 (7) $[(C_2F_5)SnBr_2]^+$; IR (gas phase): $\tilde{\nu}$=1322 (s), 1297 (m), 1223 (s), 1112 (s), 936 (s), 742 (m), 608 (w), 537 (w), 396 (w) cm^{-1}.

Bromotris(pentafluoroethyl)-1,10-phenanthrolinetin(IV) (10): Bromotris(pentafluoroethyl)stannane, $(C_2F_5)_3SnBr$, (0.18 g, 0.32 mmol) was condensed onto a solution of 1,10-phenanthroline (0.054 g, 0.30 mmol) in 3 mL of dichloromethane. After stirring for 30 h at ambient temperature all volatile components were removed under reduced pressure. The 1,10-phenanthroline complex $[(C_2F_5)_3SnBr(phen)]$ remained as a colorless microcrystalline solid (0.22 g, 0.30 mmol, 100 %). Crystals suitable for X-ray single crystal structure determination were grown from dichloromethane solution at -25 °C. ^{1}H NMR (dichloromethane/[D$_6$]acetone, 298 K): δ=8.07/8.08 (2 dd, ^{3}J(H3,H4)=8.1 Hz, ^{3}J(H3,H2)=5.1 Hz, ^{3}J(H8,H7)=8.1 Hz, ^{3}J(H8,H9)=5.1 Hz, 2H; H3/H8), 8.11 (s, 2H; H5/H6), 8.75/8.78 (2 dd, ^{3}J(H4,H3)=8.2 Hz, ^{4}J(H4,H2)=1.5 Hz, ^{3}J(H7,H8)=8.2 Hz, ^{4}J(H7,H9)=1.5 Hz, 2H; H4/H7), 9.28/9.80 ppm (2 d, ^{3}J(H2,H3)=5.1 Hz, ^{3}J(H9,H8)=5.1 Hz, 2H; H2/H9); $^{13}C\{^{1}H\}$ NMR (dichloromethane/[D$_6$]acetone, 298 K): δ=125.4/125.7 (2 s; C3/8), 127.6/127.7 (2 s; C5/6), 129.7/129.9 (2 s, C4a/C6a), 137.6/138.6 (2 s; C11/12), 141.9/142.2 (2 s, C4/7), 149.0/149.1 ppm (s; t, ^{4}J(C,F)=6 Hz; C2/9); $^{13}C\{^{19}F\}$ NMR (dichloromethane/[D$_6$]acetone, 298 K): δ=120.2 (s, ^{2}J(C,Sn)=83/87 Hz; CF_3), 120.2 (s, ^{2}J(C,Sn)=144/150 Hz; 2 CF_3), 126.1 (s; CF_2), 129.0 ppm (s; 2 CF_2); ^{19}F NMR (dichloromethane/[D$_6$]acetone, 298 K): δ=-117.8 (m, 4F; CF_2), -112.1 (m, ^{2}J(F,Sn)=330 Hz, 2F; CF_2), -81.8 (m, 6F; CF_3), -81.2 ppm (m, 3F; CF_3); $^{119}Sn\{^{1}H\}$ NMR (dichloromethane/[D$_6$]acetone, 298 K): δ=-515.1 ppm (m); IR (ATR): $\tilde{\nu}$=2961 (w), 2923 (w), 2852 (w), 1633 (w), 1591 (w), 1527 (m), 1498 (w), 1457 (w), 1434 (m), 1298 (s), 1278 (m), 1232 (w), 1196 (s), 1172 (s), 1151 (s), 1109 (m), 1074 (s), 1051 (s), 965 (w), 915 (s), 868 (m), 847 (s), 801 (m), 776 (w), 730 (s), 721 (s), 648 (w), 599 (w), 585 (w), 532 (w), 443 (w), 423 (m) cm^{-1}.

Chlorotris(pentafluoroethyl)-1,10-phenanthrolinetin(IV) (11): Chlorotris(pentafluoroethyl)stannane, $(C_2F_5)_3SnCl$, (0.54 g, 1.1 mmol) was condensed onto a solution of 1,10-phenanthroline (0.19 g, 1.1 mmol) in 3 mL of dichloromethane. After stirring for 30 h at ambient temperature all volatile components were removed under reduced pressure to give the 1,10-phenanthroline complex $[(C_2F_5)_3SnCl(phen)]$ as a colorless microcrystalline solid (0.62 g, 0.90 mmol, 82 %). Crystals suitable for X-ray single crystal structure determination were grown from dichloromethane solution at -25 °C. ^{1}H NMR (dichloromethane/[D$_6$]acetone, 298 K): δ=8.10 (m, 2H; H3/8), 8.12 (s, 2H; H5/6), 8.76/8.80 (2 d, ^{3}J(H4,H3)=8.7 Hz, ^{3}J(H7,H8)=8.7 Hz, 2H; H4/7), 9.27/9.69 ppm (2 d, ^{3}J(H2,H3)=4.8 Hz, ^{3}J(H9,H8)=4.8 Hz, 2H; H2/H9); $^{13}C\{^{1}H\}$ NMR (dichloromethane/ [D$_6$]acetone, 298 K): δ=125.6/125.8 (2 s; C3/C8), 127.5/127.8 (2 s; C5/6), 129.6/129.9 (2 s; C4a/C6a), 137.7/138.6 (2 s; C11/12), 141.8/142.2 (2 s; C3/C8), 148.8/149.0 ppm (s; t, ^{4}J(C,F)=6 Hz; C2/C9); $^{13}C\{^{19}F\}$ NMR (dichloromethane/[D$_6$]acetone, 298 K): δ=120.3 (s, ^{2}J(C,Sn)=84/87 Hz; CF_3), 120.4 (s, ^{2}J(C,Sn)=141/149 Hz; 2 CF_3), 126.9 (s; CF_2), 129.7 ppm (s; CF_2); ^{19}F NMR (dichloromethane/[D$_6$]acetone, 298 K): δ=-118.1 (m, 4F; CF_2), -112.6 (m, ^{2}J(F,Sn)=340 Hz, 2F; CF_2), -82.0 (m, 6F; CF_3), -81.7 ppm (m, 3F; CF_3); $^{119}Sn\{^{1}H\}$ NMR (dichloromethane/

[D$_6$]acetone, 298 K): δ=-489.9 ppm (m); IR (ATR): $\tilde{\nu}$=3039 (w), 1632 (w), 1589 (w), 1527 (m), 1499 (w), 1434 (m), 1353 (w), 1302 (s), 1280 (m), 1196 (s), 1173 (s), 1151 (s), 1109 (m), 1077 (s), 1051 (s), 967 (w), 917 (s), 869 (w), 847 (s), 805 (w), 776 (w), 763 (w), 731 (s), 722 (s), 670 (w), 649 (w), 620 (w), 599 (w), 586 (w), 533 (w), 480 (w), 443 (w), 424 (m) cm^{-1}.

Dibromobis(pentafluoroethyl)-1,10-phenanthrolinetin(IV) (12): Dibromobis(pentafluoroethyl)stannane, $(C_2F_5)_2SnBr_2$, (0.21 g, 0.41 mmol) was condensed onto a solution of 1,10-phenanthroline (0.054 g, 0.30 mmol) in 3 mL of dichloromethane. After stirring for 30 h all volatile components were removed under reduced pressure to give the 1,10-phenanthroline complex $[(C_2F_5)_2SnBr_2(phen)]$ as a colorless microcrystalline solid (0.21 g, 0.30 mmol, 100 %). Crystals suitable for X-ray single crystal structure determination were grown from dichloromethane solution at -25 °C. ^{1}H NMR (dichloromethane/[D$_6$]acetone, 298 K): δ=8.15 (d, d, ^{3}J(H3,H4)=8.2 Hz, ^{3}J(H3,H2)=5.1 Hz, 2H; H3/H8), 8.17 (s, 2H; H5/H6), 8.82 (d, d, ^{3}J(H4,H3)=8.2 Hz, ^{4}J(H4,H2)=1.4 Hz, 2H; H4/H7), 9.83 ppm (d, ^{3}J(H2,H3)=5.1 Hz, 2H; H2/H9); ^{13}C{^{1}H} NMR (dichloromethane/ [D$_6$]acetone, 298 K): δ=125.8 (s; C3/C8), 127.6 (s; C5/C6), 129.6 (s; C4a/C6a), 138.2 (s; C11/C12), 142.2 (s; C4/C7), 149.4 ppm (s; C2/C9); ^{13}C{^{19}F} NMR (dichloromethane/ [D$_6$]acetone, 298 K): δ=120.2 (s; CF$_3$), 123.1 ppm (s; CF$_2$); ^{19}F NMR (dichloromethane/[D$_6$]acetone, 298 K): δ=-118.7 (s, ^{2}J(F,Sn)=602/629 Hz, 4F; CF$_2$), -80.6 ppm (s, ^{3}J(F,Sn)=23 Hz, 6F; CF$_3$); ^{119}Sn{^{1}H} NMR (dichloromethane/[D$_6$]acetone, 298 K): δ=-539.8 ppm (m); IR (ATR): $\tilde{\nu}$= 3081 (w), 2962 (w), 1630 (w), 1588 (w), 1524 (m), 1494 (w), 1430 (m), 1345 (w), 1304 (s), 1280 (w), 1260 (w), 1177 (s), 1146 (m), 1086 (s), 1058 (s), 973 (w), 918 (s), 867 (m), 846 (s), 801 (m), 733 (s), 720 (s), 648 (w), 603 (w), 585 (w), 558 (w), 532 (w), 482 (w), 442 (w), 422 (m) cm^{-1}.

Dichlorobis(pentafluoroethyl)-1,10-phenanthrolinetin(IV) (13): Dichlorobis(pentafluoroethyl)stannane, $(C_2F_5)_2SnCl_2$, (0.52 g, 1.2 mmol) was condensed onto a solution of 1,10-phenanthroline (0.20 g, 1.1 mmol) in 3 mL of dichloromethane. After stirring for 16 hours all volatile components were removed under reduced pressure and the 1,10-phenanthroline complex $[(C_2F_5)_2SnCl_2(phen)]$ remained as a colorless microcrystalline solid (0.66 g, 1.09 mmol, 99 %). Crystals suitable for X-ray single crystal structure determination were grown from acetonitrile solution at -25 °C. ^{1}H NMR (acetonitrile/[D$_6$]acetone, 298 K): δ=9.00 (m, 2H; H3/H8), 9.03 (s, 2H; H5/H6), 9.76 (d (broad), ^{3}J(H4,H3)=8.2 Hz, 2H; H4/H9), 10.39 ppm (d (broad), ^{3}J(H2,H3)=5.0 Hz, 2H; H2/H9); ^{13}C{^{1}H} NMR (acetonitrile/ [D$_6$]acetone, 298 K): δ=127.2 (s; C3/C8), 128.7 (s; C5/C6), 130.6 (s; C4a/C6a), 138.4 (s; C11/C12), 144.1 (s; C4/C7), 149.7 ppm (s; C2/C9); ^{13}C{^{19}F} NMR (acetonitrile/[D$_6$]acetone, 298 K): δ=121.2 (s, ^{2}J(C,Sn)=174/182 Hz; CF$_3$), 126.3 ppm (s, ^{1}J(C,Sn)=1614/1690 Hz; CF$_2$); ^{19}F NMR (acetonitrile/[D$_6$]acetone, 298 K): δ=-119.3 (s, ^{2}J(F,Sn)=581/608 Hz, 4F; CF$_2$), -81.0 ppm (s, ^{3}J(F,Sn)=24 Hz, 6F; CF$_3$); ^{119}Sn{^{1}H} NMR (acetonitrile/[D$_6$]acetone, 298 K): δ=-474.8 ppm (quin (broad), ^{2}J(Sn,F)=614 Hz); IR (ATR): $\tilde{\nu}$=3085 (w), 1631 (w), 1608 (w), 1588 (w), 1524 (w), 1494 (m), 1430 (m), 1345 (w), 1307 (s), 1285 (m), 1177 (s), 1148 (m), 1088 (s), 1058 (s), 957 (w), 923 (s), 868 (m), 848 (s), 778 (w), 734 (m), 721 (s), 650 (w), 603 (w), 585 (w), 558 (w), 533 (w), 482 (w), 443 (w), 423 (m) cm^{-1}.

Tribromo(pentafluoroethyl)-1,10-phenanthrolinetin(IV) (14): Tribromopentafluoroethylstannane, $(C_2F_5)SnBr_3$, (0.48 g, 1.0 mmol) was condensed onto a solution of 1,10-phenanthroline (0.18 g, 1.0 mmol) dissolved in 3 mL of acetonitrile. It was heated until the white precipitate dissolved. All volatile components were removed under reduced pressure and the 1,10-phenanthroline complex $[(C_2F_5)SnBr_3(phen)]$ remained as a colorless microcrystalline solid (0.44 g, 0.67 mmol, 67 %). Crystals suitable for X-ray single crystal structure determination were grown from a hot acetonitrile solution. ^{1}H NMR (DMF/[D$_6$]acetone, 298 K): δ=8.96 (s, 2H; H5/6), 8.98 (d, d, ^{3}J(H3,H4)=8.2 Hz, ^{3}J(H3,H2)=5.2 Hz, 2H; H3/8), 9.75 (d (broad), ^{3}J(H4,H3)=8.2 Hz, 2H; H4/7), 10.32 ppm (d (broad), ^{3}J(H2,H3)=5.2 Hz, 2H; H2/9); ^{13}C{^{1}H} NMR (DMF/[D$_6$]acetone, 298 K): δ=127.3 (s, ^{3}J(Sn,C)=7 Hz; C3/8), 128.8 (s; C5/6), 130.7 (s; C4a/6a), 135.0 (s, ^{2}J(C,Sn)=15 Hz; C11/12), 144.3 (s; C4/7), 147.5 ppm (s, ^{2}J(C,Sn)=12 Hz, C2/9); ^{13}C{^{19}F} NMR (DMF/[D$_6$]acetone, 298 K): δ=120.7 (s, ^{2}J(C,Sn)=167/174 Hz, CF$_3$), 123.4 ppm (s, ^{1}J(C,Sn)=1303/1362 Hz; CF$_2$); ^{19}F NMR (DMF/[D$_6$]acetone, 298 K): δ=-120.7 (s, ^{2}J(F,Sn)=567/593 Hz, 2F; CF$_2$), -80.5 ppm (s, ^{3}J(F,Sn)=16 Hz, 3F, CF$_3$); ^{119}Sn{^{1}H} NMR (DMF/[D$_6$]acetone, 298 K): δ=-856.5 (t (broad), ^{2}J(Sn,F)=595 Hz); IR(ATR): $\tilde{\nu}$=3080 (w), 2922 (w), 2853 (w), 1629 (w), 1609 (w), 1588 (w), 1523 (m), 1495 (w), 1430 (s), 1343 (w), 1321 (w), 1298 (m), 1277 (w), 1225 (w), 1205 (s), 1176 (s), 1150 (m), 1105 (m), 1081 (s), 1051 (s), 969 (w), 916 (s), 869 (w), 847 (s), 778 (w), 735 (m), 726 (m), 717 (s), 650 (m), 600 (w), 582 (w), 559 (w), 543 (w), 532 (w), 510 (w), 483 (w), 445 (w), 425 (m) cm^{-1}.

(η^{1}-Cyclopentadienyl)tris(pentafluoroethyl)stannane (15): Sodium cyclopentadienide (123 mg, 1.41 mmol) and a sample of bromotris(pentafluoroethyl)stannane (754 mg, 1.36 mmol) were loaded into a Young valve ampoule. After stirring at ambient temperature for 1 d highly volatile compounds were removed in a static vacuum. By condensation at ambient temperature and $1\cdot10^{-3}$ mbar $(C_2F_5)_3SnCp$ was obtained as a yellow oil (0.56 g, 1.0 mmol, 76 %). ^{1}H NMR ([D]chloroform, 298 K): δ=6.39 ppm (s, ^{2}J(H,Sn)=34 Hz; C$_5$H$_5$); ^{13}C{^{1}H} NMR ([D]chloroform, 298 K): δ=115.0 ppm (s, ^{1}J(C,Sn)=41 Hz; C$_5$H$_5$); ^{13}C{^{19}F} NMR: δ=119.5 (s, ^{2}J(C,Sn)=81/85 Hz; CF$_3$), 126.0 ppm (s, ^{1}J(C,Sn)=482/504 Hz; CF$_2$); ^{19}F NMR ([D]chloroform, 298 K): δ=-110.1 (s, ^{2}J(F,Sn)=310/324 Hz; CF$_2$), -83.1 ppm (s; CF$_3$); ^{119}Sn{^{19}F} NMR ([D]chloroform, 298 K): δ =-203.8 ppm (sext, ^{2}J(Sn,H)=35 Hz); ^{119}Sn{^{1}H} NMR ([D]chloroform, 298 K): δ=-203.8 ppm (sept, dec, ^{2}J(F,Sn)=324 Hz, ^{3}J(F,Sn)=4 Hz); MS (EI, 70 eV.) {m/z (%) [assignment]}: 49.0 (40), 51.0 (14), 65.0 (20) [Cp]$^{+}$, 84.0 (27) [CpF]$^{\cdot+}$, 85.9 (18), 100.0 (5) [C$_2$F$_4$]$^{\cdot+}$, 127.0 (13), 138.9 (8) [SnF]$^{+}$, 184.9 (100) [SnCp]$^{+}$, 222.9 (11) [SnF$_2$Cp]$^{+}$, 322.9 (6) [(C$_2$F$_5$)SnFCp]$^{+}$, 422.9 (11) [(C$_2$F$_5$)$_2$SnCp]$^{+}$, 541.9 (4) [(C$_2$F$_5$)$_3$SnCp]$^{\cdot+}$; IR (ATR): $\tilde{\nu}$=1464 (w), 1384 (w), 1312 (s), 1293 (m), 1191 (s), 1088 (s), 1022 (w), 982 (w), 928 (s), 908 (m), 816 (w), 755 (s), 738 (s), 648 (m), 603 (m), 587 (w), 560 (w), 535 (w), 430 (w) cm^{-1}.

10.1002/chem.201701270

Table 3. Crystal data and refinement characteristics for [$(C_2F_5)_3$SnBr(phen)], [$(C_2F_5)_2$SnBr$_2$(phen)], [$(C_2F_5)_3$SnCl(phen)], [$(C_2F_5)_2$SnCl$_2$(phen)], [(C_2F_5)SnBr$_3$(phen)] and $(C_2F_5)_3$SnCp.

	[$(C_2F_5)_3$SnBr(phen)][a]	[$(C_2F_5)_2$SnBr$_2$(phen)]	[$(C_2F_5)_3$SnCl(phen)][b]	[$(C_2F_5)_2$SnCl$_2$(phen)]	[(C_2F_5)SnBr$_3$(phen)]	$(C_2F_5)_3$SnCp
	10	**12**	**11**	**13**	**14**	**15**
Crystallographic Section						
empirical formula	$C_{18}H_8BrF_{15}N_2Sn$	$C_{16}H_8Br_2F_{10}N_2Sn$	$C_{18}H_8ClF_{15}N_2Sn$	$C_{16}H_8Cl_2F_{10}N_2Sn$	$C_{14}H_8Br_3F_5N_2Sn$	$C_{11}H_5F_{15}Sn$
F(000)	1400	2624	1328	2336	1224	1024
a / pm	988.99(2)	1625.1(1)	988.03(2)	1612.33(2)	896.41(1)	895.36(2)
b / pm	1010.56(2)	1498.6(3)	1005.95(2)	1469.47(2)	1195.00(2)	1368.17 (2)
c / pm	2297.20(6)	1649.8(2)	2290.71(6)	1626.26(3)	1634.84(3)	1305.74(2)
α / °	90	90	90	90	90	90
β / °	98.254(1)	90	98.236(2)	90	90.835(1)	91.938(2)
γ / °	90	90	90	90	90	90
V / $10^6 \cdot Å^3$	2272.11(9)	4017.9(8)	2253.28(9)	3853.05(10)	1751.07(5)	1598.63(4)
Z	4	8	4	8	4	4
ρ / g·cm^{-3}	2.151	2.304	2.038	2.096	2.495	2.247
crystal system	monoclinic	orthorhombic	monoclinic	orthorhombic	monoclinic	monoclinic
space group	$P2_1/n$	*Pbca*	$P2_1/n$	*Pbca*	$P2_1/n$	$P2_1/n$
shape / color	colorless fragment	colorless column	colorless fragment	colorless fragment	colorless fragment	colorless cylindricall
crystal size/ mm^3	0.30 x 0.20 x 0.10	0.30 x 0.10 x 0.10	0.30 x 0.29 x 0.07	0.30 x 0.24 x 0.04	0.30 x 0.25 x 0.25	0.3 × 0.2 × 0.2
Data collection						
diffractometer	Kappa CCD					SuperNova
T / K	100(2)	100(2)	100(2)	100(2)	100(2)	90.0(1)
theta range [°]	2.94 / 27.48	3.08 / 30.00	2.95 / 27.48	3.13 / 30.00	3.41 / 30.00	2.72 to 30.03
index range	-12<=h<=12 -13<=k<=13 -29<=l<=29	-22<=h<=22 -21<=k<=21 -23<=l<=22	-12<=h<=12 -13<=k<=13 -29<=l<=29	-22<=h<=22 -20<=k<=20 -22<=l<=22	-12<=h<=12 -16<=k<=16 -22<=l<=22	-12<=h<=12 -19<=k<=19 -18<=l<=18
total data collected	34985	85908	9991	91422	40873	101043
unique data	5189	5849	5157	5597	5096	4675
observed data ($I > 2\sigma$)	4619	4648	4239	4948	4380	4539
R(int) / *R*(σ)	0.049	0.0867	0.0259	0.060	0.084	0.0400
μ / mm^{-1}	3.016	5.347	1.387	1.704	8.354	1.755
R_1 / wR_2 [$I>2\sigma(I)$]	0.0427 / 0.0943	0.0314 / 0.0606	0.0429 / 0.0879	0.0404 / 0.1040	0.0414 / 0.1113	0.0239 / 0.0522
R_1 / wR_2 (all data)	0.0502 / 0.0971	0.0502 / 0.0671	0.0563 / 0.0927	0.0455 / 0.1070	0.0498 / 0.1159	0.0250 / 0.0527
goodness of fit (S_{all})	1.131	1.078	1.068	1.104	1.061	1.205
$\Delta\rho_{max/min}$ / e Å^{-3}	3.625 / -1.928	1.001 / -0.771	3.622 / -1.989	4.371 / -1.361	1.317 / -1.535	1.08/-0.38
CCDC number	1003536	1003538	1003537	1003539	10035340	1003540

[a] Compound 10 shows a disorder of the bromine with on C_2F_5 ligand in ratio 89:11; [b] Compound 11 shows a disorder of the chlorine with on C_2F_5 ligand in ra
90:10.

Acknowledgements

This work was financially supported by Merck KGaA (Darmstadt, Germany) and Solvay (Hannover, Germany) which is gratefully acknowledged. We acknowledge the support by the Deutsche Forschungsgemeinschaft (Core Facility GED@BI, Mi477/21-1) and we thank Prof. Dr. Lothar Weber and Dr. Julia Bader for helpful discussions.

Keywords: fluorine • halogene • pentafluoroethyl • stannane • perfluoroalkyl

[1] R. Eujen, U. Thurmann, *J. Organomet. Chem.* **1992**, *433*, 63–77.
[2] N. Jahn, PhD Thesis, Bergische Universität – Gesamthochschule Wuppertal, **1994**.
[3] W. R. Cullen, J. R. Sams, M. C. Waldman, *Inorg. Chem.* **1970**, *9*, 1682–1686.
[4] H. D. Kaesz, J. R. Phillips, F. G. A. Stone, *J. Am. Chem. Soc.* **1960**, *82*, 6228–6232.
[5] K. Kawakami, H. Kuivila, *J. Org. Chem.* **1969**, *34*, 3715–3716.
[6] J. R. Falck, J.-Y. Lai, D. Ramana, S.-G. Lee, *Tetrahedron Lett.* **1999**, *40*, 2715–2718.
[7] H. Lange, D. Naumann, *J. Fluorine Chem.* **1984**, *26*, 93–95.
[8] J. Mehrabani, PhD Thesis, Universität zu Köln, **2004**.
[9] a) M. Henrich, A. Marhold, A. Kolomeitsev, A. Kadyrov, G.-V. Röschenthaler, J. Barten, DE 101 28 703 A 1, **2001**; b) M. H. Königsmann, PhD Thesis, Universität Bremen, Bremen, **2005**; c) B. Waerder, S. Steinhauer, B. Neumann, H.-G. Stammler, A. Mix, Y. V. Vishnevskiy, B. Hoge, N. W. Mitzel, *Angew. Chem. Int. Ed.* **2014**, *53*, 11640; d) B. Waerder, S. Steinhauer, B. Neumann, H.-G. Stammler, A. Mix, Y. V. Vishnevskiy, B. Hoge, N. W. Mitzel, *Angew. Chem.* **2014**, *126*, 11824.
[10] C. A. Tolman, *Chem. Rev.* **1977**, *77*, 313–348.
[11] S. A. Hayes, R. J. F. Berger, B. Neumann, N. W. Mitzel, J. Bader, B. Hoge, *Dalton Trans.* **2010**, *39*, 5630.
[12] U. H. G. Thurmann, PhD Thesis, Bergische Universität – Gesamthochschule Wuppertal, **1989**.
[13] F. Dörrenbach, PhD Thesis, Bergische Universität – Gesamthochschule Wuppertal, **1989**.
[14] Z.-H. Su, B.-B. Zhou, Z.-F. Zhao, S.W. Ng, *Acta Cryst.* **2007**, *E63*, 394-395.
[15] M. A. Buntine, V. J. Hall, F. J. Kosovel, E. R. T. Tiekink, *J. Phys. Chem. A* **1998**, *102*, 2472–2482.
[16] R. Eujen, N. Jahn, U. H. G. Thurmann, *J. Organomet. Chem.* **1992**, *434*, 159–168.
[17] H.-O. Kalinowski, S. Berger, S. Braun, *^{13}C-NMR-Spektroskopie;* Georg Thieme, Stuttgart, **1984**.
[18] G. M. Sheldrick, *Acta Cryst.* **2008**, *64*, 112–122.

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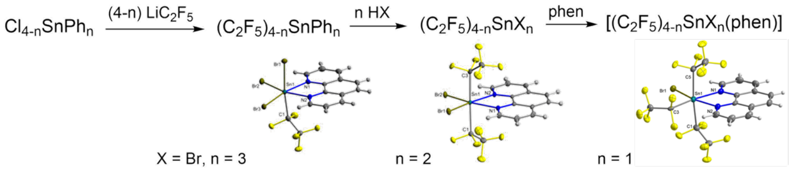

In this contribution, we present a convenient protocol for the high yield synthesis of (pentafluoroethyl)stannanes (n = 1-3) by using LiC_2F_5. (Pentafluoroethyl)phenylstannanes are functionalized by gaseous hydrogen halides HX (X = Cl, Br) to give (pentafluoroethyl)tin halides, their corresponding 1,10-phenanthroline (phen) complexes were structurally characterized by X-ray diffraction analysis.

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Synthesis of Mono-, Bis- and Tris(pentafluoroethyl)tin Derivatives, $(C_2F_5)_{4-n}SnX_n$ (X = Ph, Me, Cl, Br, Cp; n = 1-3)